

Figure 1. Gas phase infrared spectra of metal borohydrides.

the same conclusion. The metal atom positions in $\text{Pu}(\text{BH}_4)_4$ are closely related to those in solid $\text{U}(\text{BH}_4)_4$, but are more symmetrical. The structure can be converted into the $\text{Zr}(\text{BH}_4)_4$ -type structure with little distortion if molecules at $1/2, 1/2, 1/2$ are moved to $1/2, 1/2, 0$.

The room temperature gas phase IR spectra of hafnium, neptunium, and plutonium borohydrides (Figure 1) were taken on a Perkin-Elmer 283 IR spectrophotometer with the sample contained in a 10-cm cell fitted with KBr windows. It can be seen that the Np and Pu compounds have similar spectra to that of $\text{Hf}(\text{BH}_4)_4$ in which four BH_4^- groups surround the metal in a tetrahedral array each coordinated via three hydrogen bridge bonds making the metal 12 coordinate.⁹

Our preliminary Raman spectrum on solid $\text{Np}(\text{BH}_4)_4$ at -85°C is equivalent to that for single-crystal $\text{Hf}(\text{BH}_4)_4$ ^{9a} if one allows for effects due to the heavier Np atom. This reinforces our belief that $\text{Np}(\text{BH}_4)_4$ is a monomer in the solid state. Since polymeric linkages need not be broken upon vaporizing, $\text{Np}(\text{BH}_4)_4$ and $\text{Hf}(\text{BH}_4)_4$ therefore have much higher vapor pressures than $\text{U}(\text{BH}_4)_4$ which was shown to be a monomer and of the same structure as $\text{Hf}(\text{BH}_4)_4$ in the gaseous state.^{9b,10}

The physical properties of the known actinide(IV) borohydrides are summarized in Table I.

Further studies are underway on the spectroscopic, structural, and magnetic properties of these new actinides borohydrides.

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Synthesis, Structure, and Spectral Properties of $(\text{TFF})(\text{HgCl}_3)$, an Unusual Metallothetraethylen

Sir:

Extensive investigations into the chemical and physical properties of low-dimensional organic materials have identified tetrathiafulvalene (TFF) as one of the major components of such systems. These materials are currently of great interest because of the demonstration of the existence of a one-dimensional metallic state.^{1,2}

While there have been numerous studies devoted to purely organic charge-transfer salts, of which $(\text{TFF})(\text{TCNQ})$ is exemplary, considerably less attention has centered on inorganic salts of TTF.³⁻⁵

We report here the preparation and characterization of the trichloromercurate(II) salt of the TTF cation radical, $(\text{TTF})(\text{HgCl}_3)$, **1**. In this solid, we observe three independent TTF cation radicals, one having only C_1 crystallographic symmetry and two others with their centroids coincident with crystallographic centers of symmetry. Further, there are two distinctive chloromercurate(II) species: one a dimeric edge-bridged bitetrahedron $(\text{HgCl}_3)_2^{2-}$ and the other a polymeric species $(\text{HgCl}_3)_n^{n-}$ in which the coordination geometry is best described as trigonal bipyramidal.

Oxidation of tetrathiafulvalene with mercuric chloride in acetonitrile produced **1** and Hg_2Cl_2 . Black, lustrous crystals were obtained from acetonitrile. Crystal data: $a = 12.661$ (3), $b = 15.969$ (4), $c = 7.416$ (2) Å; $\alpha = 98.69$ (2), $\beta = 95.73$ (2), $\gamma = 120.01$ (2)°; $V = 1256.2$ Å³; $Z = 4$ (for $(\text{TTF})(\text{HgCl}_3)$), space group $P1$. Intensity data for 4298 independent reflections were collected employing monochromated Mo $K\alpha$ radiation and the θ - 2θ scan technique. The data were corrected for the usual geometric factors as well as absorption effects. The structure was solved by Patterson and Fourier methods and has been refined by the least-squares technique (anisotropic refinement for the nonhydrogen atoms and inclusion, but no refinement of the hydrogen atoms) to a final R_F value of 0.08.

Some aspects of the structure of $(\text{TTF})(\text{HgCl}_3)$ are illustrated in Figure 1. Qualitatively, the structure can be separated into two types of two-dimensional layers. One of these layers (centered about $y = 0.0$) contains both inorganic and organic polymers propagating along the crystallographic c axis, Figure 1. The covalent inorganic polymer contains roughly trigonal bipyramidal coordination about the Hg(II) with equatorial Hg-Cl bond lengths ranging from 2.374 (5) to 2.545 (5) Å. The two axial bond lengths are considerably longer at 2.982 (5) and 3.112 (5) Å. The structural repeat unit is HgCl_3^- with both axial ligands also involved in equatorial interactions. Colinear with this covalent inorganic polymer is a columnar array of TTF^+ radical cations, Figure 1. The molecular overlap

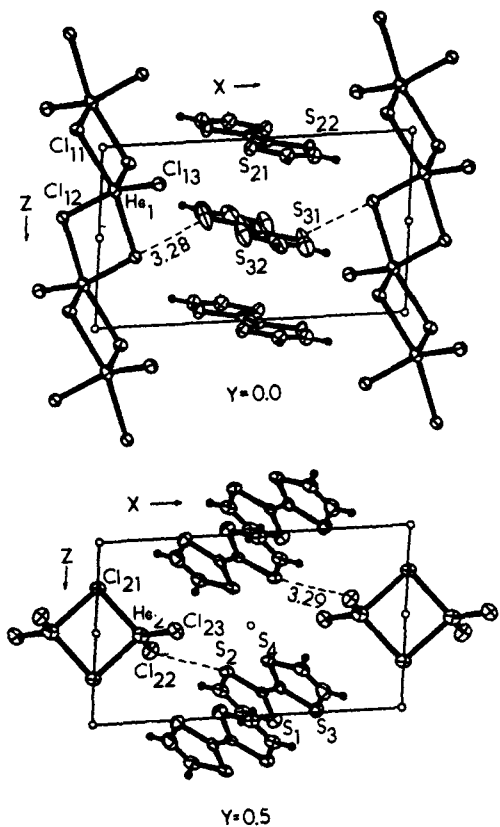


Figure 1. The structure of (TTF)(HgCl₃). The $y = 0.0$ projection illustrates the polymeric HgCl species and ring-over-bond TTF columns, while the $y = 0.5$ projection shows the Hg₂Cl₆ units and eclipsed TTF dimers. Short Cl...S contacts, one in each layer, are noted.

in this columnar array is approximately of the ring-over-bond type found in (TTF)(TCNQ)⁶ and many of its derivatives. The mean separation of molecular planes is on the order of 3.6 Å and is considerably longer than that observed in (TTF)(TCNQ) (3.48 Å)⁶ but similar to the eclipsed columnar spacings found in (TTF)Cl_{0.92} (3.59 Å)⁷ and (TTF)Br_{0.79} (3.57 Å).⁸

The second of these layers (centered about $y = 0.5$) contains solely dimeric species, Figure 1. The chloromercurate(II) entity is a dimeric, edge-shared bitetrahedron with Hg-Cl bond lengths of 2.600 (5) and 2.696 (5) Å for the bridging ligands and 2.368 (5) and 2.381 (5) Å for the terminal ligands. Coupled with these inorganic dimers are pairs of TTF⁺ cations strongly associated about centers of symmetry, Figure 1. The mean separation in these organic dimers is short at 3.43 Å (vide supra) and the molecular overlap is nearly eclipsed with a slight lateral shift. This spacing is identical with that found in the dimeric salt (TTF)Br_{1.0}.⁹

Clearly, **1** is unusual on account of the presence in one crystal of both dimeric and polymeric HgCl units and of two types of TTF aggregates. Ring-over-bond columns are observed in partially oxidized TTF derivatives, i.e., TTFⁿ⁺ ($n < 1$),^{2,6-8} while eclipsed dimers have been reported in the fully oxidized derivatives (TTF)Br⁹ and (TTF)Cl² in which $n = 1$. The x-ray data thus imply that **1** contains TTF in two different oxidation states.¹⁰

We have previously reported that the ν_3 mode in TTF undergoes large frequency shifts on oxidation of the thiocarbon to the +1 and +2 states.³ The resonance Raman spectrum of **1**, obtained using 4579-Å excitation, Figure 2, reveals two bands in a 1:1 ratio at 1415 and 1424 cm⁻¹ which we believe reflects the presence of two different kinds of TTF moieties, distinguished by a small difference in degree of charge transfer, which is consistent with the crystallographic data. Such a splitting has not been observed in numerous other metallo-

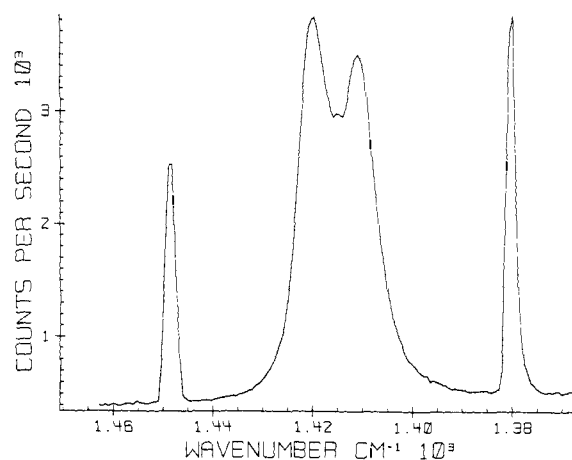


Figure 2. Resonance Raman spectrum of powdered (TTF)(HgCl₃).

tetraethylenes studied in these laboratories. These results suggest that resonance Raman spectroscopy will be useful in probing subtle features of electron distribution in charge-transfer salts.

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- (10) It is difficult to express this difference quantitatively but it may be estimated to be $< 0.2e$.
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Powerful Anchimeric Effect of the *N*-Nitroso Group

Sir:

We wish to report the exceptionally powerful neighboring-group effect of the *N*-nitroso group in the solvolysis of derivatives of β -hydroxydialkylnitrosamines.

In an earlier study, we¹ reported the very rapid rate of hydrolysis of the urea functionalities in α -ureidonitrosamines.